Biogeosciences, 12, 6389–6403, 2015
www.biogeosciences.net/12/6389/2015/
doi:10.5194/bg-12-6389-2015

Biogeosciences Open Access EGU

C : N : P stoichiometry at the Bermuda Atlantic Time-series Study station in the North Atlantic Ocean

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Received: 28 May 2015 – Published in Biogeosciences Discuss.: 19 June 2015
Revised: 30 September 2015 – Accepted: 23 October 2015 – Published: 9 November 2015

Abstract. Nitrogen (N) and phosphorus (P) availability, in addition to other macro- and micronutrients, determine the strength of the ocean's carbon (C) uptake, and variation in the N : P ratio of inorganic nutrient pools is key to phytoplankton growth. A similarity between C : N : P ratios in the plankton biomass and deep-water nutrients was observed by Alfred C. Redfield around 80 years ago and suggested that biological processes in the surface ocean controlled deep-ocean chemistry. Recent studies have emphasized the role of inorganic N : P ratios in governing biogeochemical processes, particularly the C : N : P ratio in suspended particulate organic matter (POM), with somewhat less attention given to exported POM and dissolved organic matter (DOM). Herein, we extend the discussion on ecosystem C : N : P stoichiometry but also examine temporal variation in stoichiometric relationships. We have analyzed elemental stoichiometry in the suspended POM and total (POM + DOM) organic-matter (TOM) pools in the upper 100 m and in the exported POM and subeuphotic zone (100–500 m) inorganic nutrient pools from the monthly data collected at the Bermuda Atlantic Time-series Study (BATS) site located in the western part of the North Atlantic Ocean. C : N and N : P ratios in TOM were at least twice those in the POM, while C : P ratios were up to 5 times higher in TOM compared to those in the POM. Observed C : N ratios in suspended POM were approximately equal to the canonical Redfield ratio (C : N : P = 106 : 16 : 1), while N : P and C : P ratios in the same pool were more than twice the Redfield ratio. Average N : P ratios in the subsurface inorganic nutrient pool were ∼ 26 : 1, squarely between the suspended POM ratio and the Redfield ratio. We have further linked variation in elemental stoichiometry to that of phytoplankton cell abundance observed at the BATS site. Findings from this study suggest that elemental ratios vary with depth in the euphotic zone, mainly due to different growth rates of cyanobacterial cells. We have also examined the role of the Arctic Oscillation on temporal patterns in C : N : P stoichiometry. This study strengthens our understanding of the variability in elemental stoichiometry in different organic-matter pools and should improve biogeochemical models by constraining the range of non-Redfield stoichiometry and the net relative flow of elements between pools.

1 Introduction

Nitrogen (N) and phosphorus (P) are critical elements that control primary production in large portions of the surface ocean. Traditionally, N is considered a proximate and P is an ultimate limiting nutrient in surface waters (Tyrrell, 1999), but primary production in the North Atlantic Ocean has been suggested to be P stressed (Wu et al., 2000; Karl et al., 2001; Sañudo-Wilhelmy et al., 2001; Lomas et al., 2010). Alfred C. Redfield first noted the similarity between N : P ratios in surface ocean particulate organic matter (POM) and in deep-water inorganic nutrients; this observation was further extended to include carbon (Redfield, 1934). Oceanographic studies have consistently found mean plankton biomass to adhere to the Redfield ratio (C : N : P = 106 : 16 : 1; Redfield, 1958; Copin-Montegut and Copin-Montegut, 1983; Geider

and La Roche, 2002), and since then this ratio has become a fundamental tenet in marine biogeochemistry. Deviations from the canonical ratio have been used to provide insights into phytoplankton physiology (Goldman et al., 1979; Quigg et al., 2003), nutrient limitation of primary production (e.g., Falkowski and Raven, 1997; Moore et al., 2013), efficiency of biological carbon sequestration in the ocean (Sigman and Boyle, 2000) and the input–output balance of the marine N cycle (e.g., Gruber and Sarmiento, 1997). Geochemists use the Redfield conceptual model to determine the state of the marine N cycle using the N* proxy (e.g., Gruber and Sarmiento, 1997). In the context of this proxy, subsurface nutrient N : P ratios $> 16:1$ suggest net nitrogen gain, while ratios $< 16:1$ suggest net nitrogen loss (e.g., Gruber and Deutsch, 2014). However, this relatively simple point of view has been shown to yield N_2 fixation rates that are overestimated by up to 4 times when compared to directly measured rates (Mills and Arrigo, 2010). In part, this overestimation is due to the production and sedimentation of non-N_2 fixer biomass that can occur at ratios much greater than the Redfield ratio, particularly in the subtropical and tropical oceans (Singh et al., 2013; Martiny et al., 2013; Teng et al., 2014). Furthermore, an ocean circulation model has shown that the N : P ratio of biological nutrient removal varies geographically, from 12 : 1 in the polar ocean to 20 : 1 in the subantarctic zone, regions where N_2 fixation is not thought to be important (Weber and Deutsch, 2010). With a better understanding of N cycle processes, the validity of the Redfield model for nutrient uptake has been questioned (Sañudo-Wilhelmy et al., 2004; Mills and Arrigo, 2010; Zamora et al., 2010).

Biologically speaking, a fixed N : P ratio, like the Redfield ratio, would suggest that nutrients are taken up in that ratio during the production of new organic matter (Redfield, 1958; Lenton and Watson, 2000). This conceptual model has been challenged by the fact that the variability in nutrient requirements is related to the functioning and evolution of microbes (Arrigo, 2005). The N : P ratio in phytoplankton need not be in the canonical ratio and can vary widely from coastal upwelling to transitional to oligotrophic regions of the ocean. The observed ratio varies with taxa and growth conditions (Arrigo et al., 1999; Quigg et al., 2003; Klausmeier et al., 2004). For example, it has been shown that non-Redfield nutrient utilization is common during blooms (Arrigo et al., 1999) and in regions dominated by cyanobacteria (Martiny et al., 2013). The N : P ratio of *Synechococcus* and *Prochlorococcus*, small and abundant phytoplankton cells in the open ocean, varies from 13.3 to 33.2 and 15.9 to 24.4, respectively, during exponential growth, while the ratio can be as high as 100 during PO_4^{3-}-limited growth (Bertilsson et al., 2003; (Heldal et al., 2003). Another cyanobacteria, the N_2 fixer *Trichodesmium* has an N : P ratio that varies from 42 to 125 (Karl et al., 1992), while in general diatoms have a ratio of $\sim 11:1$ (Quigg et al., 2003; Letelier and Karl, 1996; Mahaffey et al., 2005). Excess downward dissolved organic nitrogen (DON) fluxes relative to NO_3^- are associated with *Trichodesmium* abundance (Vidal et al., 1999). Thus the relative abundance of different phytoplankton functional groups may lead to coupling of N and P cycles in non-Redfieldian proportions.

Considerable effort has been made to understand the variability and controls on the N : P ratio in the dissolved inorganic nutrient pool (e.g., Gruber and Sarmiento, 1997; Pahlow and Riebesell, 2000; Arrigo, 2005). In contrast, analysis of C : N : P ratios, in particulate organic matter (POM) and dissolved organic matter (DOM), are more scarce (Karl et al., 2001; Letscher et al., 2013). The C : N : P ratio, however, has great relevance in oceanography, as it connects the "currency" of the ocean, i.e., carbon, to some of its controlling variables (N and P). Here, we present a detailed analysis of C : N : P stoichiometry of POM and TOM along with N : P stoichiometry of dissolved inorganic nutrients at the Bermuda Atlantic Time-series Study (BATS) for an 8-year period. The observed ratios are correlated with and discussed in the context of co-measured biological parameters such as cell abundances of different phytoplankton groups and chlorophyll *a*. The goal of this study was to quantitatively assess C : N : P ratios in all (POM, TOM and inorganic nutrients) the pools and the ratios' deviations from the Redfield ratio, and relationships to biogeochemical cycling.

2 Methods

2.1 Data availability

Since 1988, the BATS site, located in the western subtropical North Atlantic Ocean (31°40′ N, 64°10′ W), has provided a relatively unique time-series record of nutrient biogeochemical cycles. However, data on total organic C (TOC), total organic N (TON) and total organic P (TOP) and on particulate organic C (POC), particulate organic N (PON), and particulate organic P (POP) have only been collected concurrently since 2004. These data were collected from seven different depths (5, 10, 20, 40, 60, 80 and 100 m) over the euphotic zone. We obtained these data from the BATS website (bats.bios.edu) and analyzed the data record from 2004 to 2012.

2.2 Analytical methods

Samples for nitrate (NO_3^-) and phosphate (PO_4^{3-}) were gravity filtered (0.8 µm) and frozen (-20°C) in HDPE bottles until analysis (Dore et al., 1996). NO_3^- and PO_4^{3-} were measured using a Technicon autoanalyser with an estimated inaccuracy of ~ 0.12 and $0.02\,\mu mol\,kg^{-1}$, respectively (Bates and Hansell, 2004). The Magnesium Induced Co-precipitation (MAGIC) soluble reactive P (SRP) method (Karl and Tein, 1997) was used starting in late 2004 to improve both the sensitivity and the accuracy of the inorganic PO_4^{3-} analysis (Lomas et al., 2010). POC and PON samples were filtered

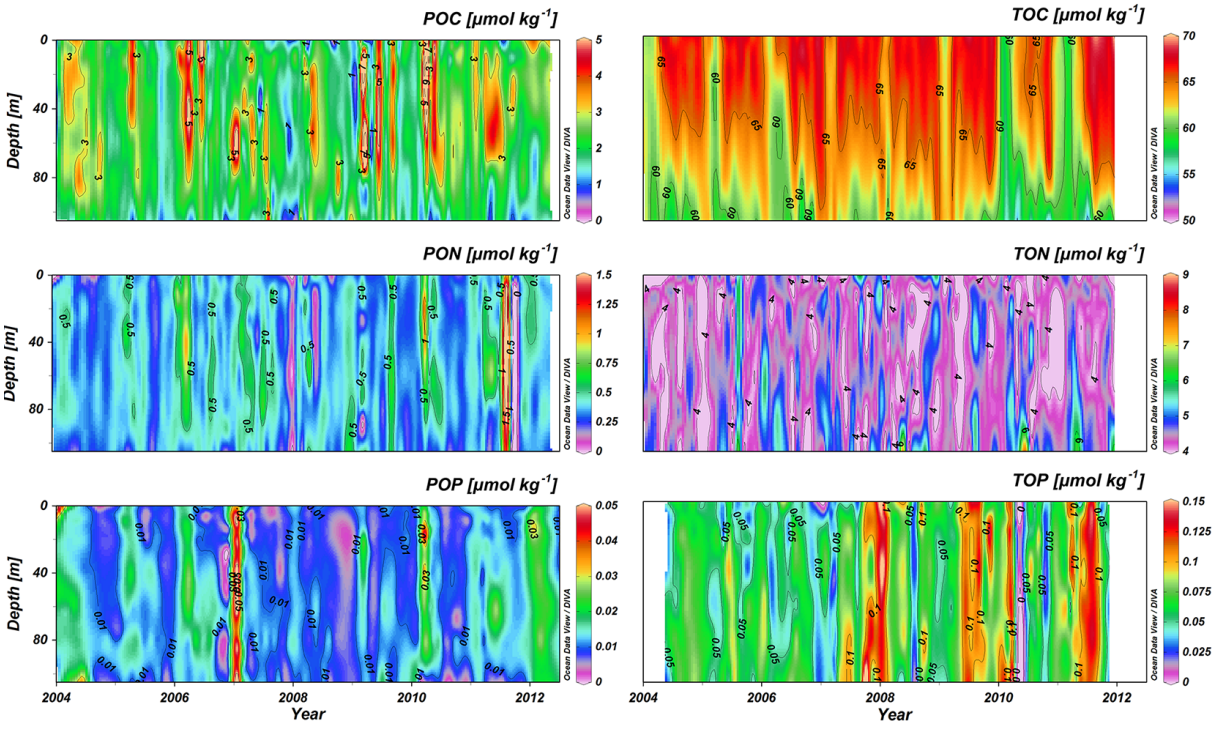

Figure 1. Monthly BATS data on C, N and P in total and particulate organic matter in the top 100 m from January 2004 to April 2012.

on pre-combusted (450 °C, 4 h) Whatman GF/F filters (nominal pore size 0.7 µm) and frozen (−20 °C) until analysis on a Control Equipment 240-XA or 440-XA elemental analyzer (Steinberg et al., 2001; Lomas et al., 2013). POP was analyzed using the ash-hydrolysis method with oxidation efficiency and standard recovery checks (Lomas et al., 2010). TOC and TON concentrations were determined using high-temperature combustion techniques (Carlson et al., 2010). Total P (TP) concentrations were quantified using a high-temperature persulfate oxidation technique and TOP calculated by subtraction of the MAGIC-SRP value (Lomas et al., 2010). Ideally, DOM concentrations would have been estimated by subtracting POM from its total organic concentrations, e.g., [DOC] = [TOC] − [POC], but we did not have paired TOC (and TON) and POC (and PON) values; corresponding POC (and PON) values were taken at slightly different depths but on the same sampling day. Nevertheless, subtraction would not have had a substantial impact because, on average, POC and PON values in the upper 100 m were < 4 % of TOC and TON, respectively (Fig. 1). Both the accuracy and precision of dissolved organic compound concentrations decrease with depth as concentrations of inorganic nutrients increase to dominate the total pools.

Chlorophyll *a* pigments were analyzed by HPLC using the method of van Heukelem and Thomas (2001). Samples for flow cytometric enumeration of pico- and nanoplankton were collected on each cruise and analyzed as described in Lomas et al. (2013). Export fluxes of POC, PON and POP were estimated using surface-tethered particle interceptor traps deployed at a depth of 200 m as described in previous publications (Lomas et al., 2010; Steinberg et al., 2001). Elemental masses of material captured in sediment traps, trap collection surface area and deployment length were used to calculate fluxes (see Lomas et al., 2013, for a more detailed methodology on all the described parameters Sect. 2, "Methods").

2.3 Data processing

Our POM and TOM analysis was restricted to the upper 100 m, which also reflects the approximate mean depth of the euphotic zone at BATS (Siegel et al., 2001) and the zone where nutrients are depleted to near analytical detection. All data presented as elemental ratios are in mol per mol units. Mixed layer depth was defined as a 0.125 kg m^{-3} difference in seawater density from the surface (Gardner et al., 1995). While mixed layer depths (MLDs) were always deepest during winter, the exact timing of the deepest mixing shifted between years. For example, during 2005, the MLD was deepest in March, while it was deepest during February in 2006 (Fig. 3). Therefore, when presenting data on an annual cycle, we aligned our data to the measured timing of deep mixing in each year and combined all the data to a single 12-month composite (e.g., Carlson et al., 2009). Generally the mixed layer depth was no deeper than ~ 25 m in summer; thus, we used this depth range (0–25 m) to represent the "surface" data and present our analysis in two depth bins: 0–25 and 25–100 m.

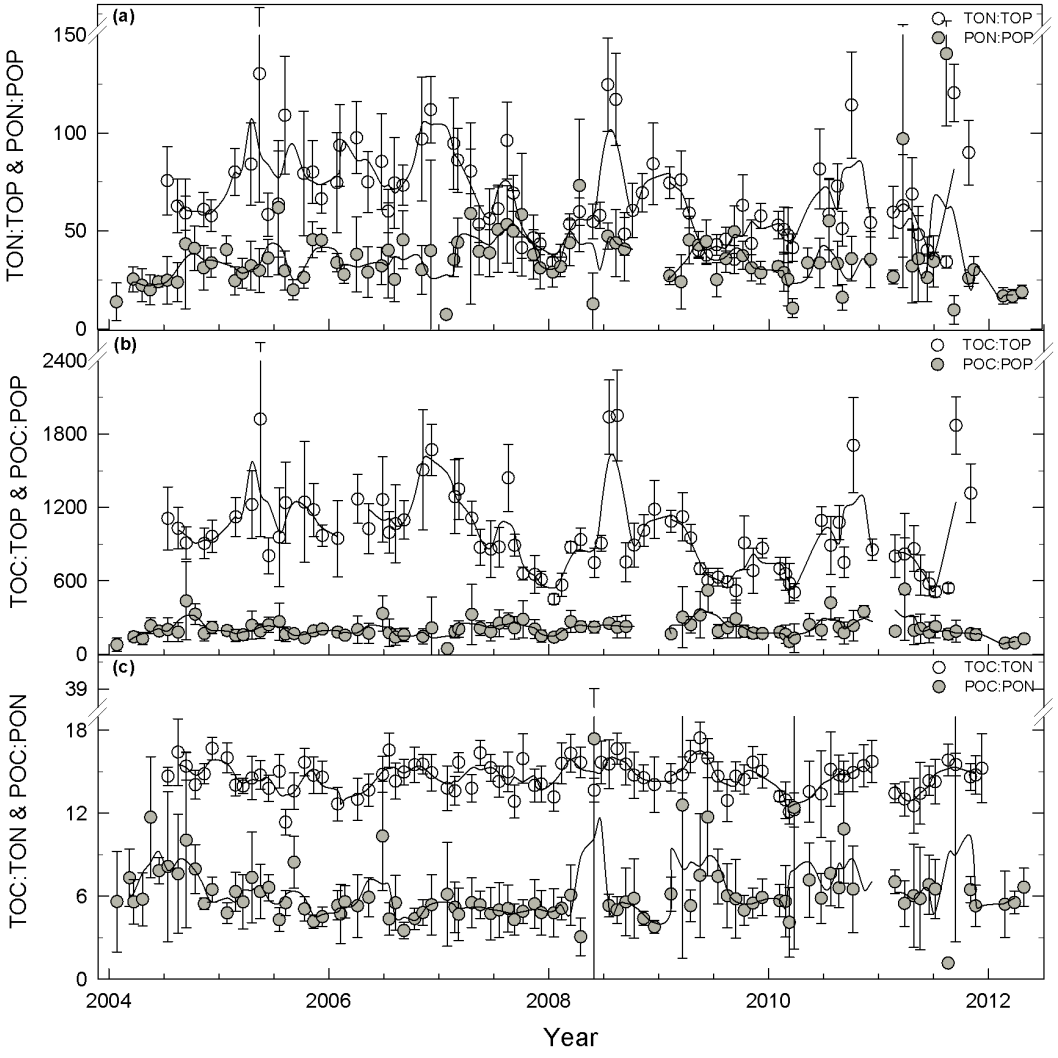

Figure 2. Monthly stoichiometry during 2004–2010 at 0–100 m. Solid lines are 3-month running means. Error bars are 1σ from the mean values.

3 Results

We present time-series data of chemical constituents in POM and TOM pools (Fig. 1). We further calculated depth-averaged ratios of the chemical constituents. We first calculated the average concentration of each element over the depth segment (e.g., 0–25 m) and then calculated the ratios based upon those averages. Over the entire length of the time series, euphotic zone TON : TOP ratios varied between 34 and 130 (Fig. 2a), while TOC : TOP ratios varied between 450 and 1952 (Fig. 2b) and TOC : TON varied between 11 and 17 (Fig. 2c).

Suspended euphotic zone PON : POP ratios were generally lower than TON : TOP ratios (Fig. 2, Table 1). The PON : POP ratio ranged from 7 to 140. Similarly POC : POP ratios were much lower than TOC : TOP, varying from 45 to 532. The POC : PON ratio ranged between 1 and 19. Elemental ratios in TOM and POM were significantly greater than the Redfield ratio ($p < 0.05$; z test) with the exception of the POC : PON ratio.

3.1 Annual patterns

3.1.1 Concentrations of POM and TOM

There were annual oscillations in POM pools in the upper 100 m (Fig. 1). TOC also showed annual oscillations; however, TON concentrations were relatively constant throughout the study period. The pattern of TOP showed an increasing trend from early 2007 until early 2008 ($\mathrm{TOP} = 0.0936 \times \text{decimal year} - 187.8$; $r^2 = 0.77$, $p < 0.05$). However, there were no long-term sustained changes in the concentration of POM and TOM.

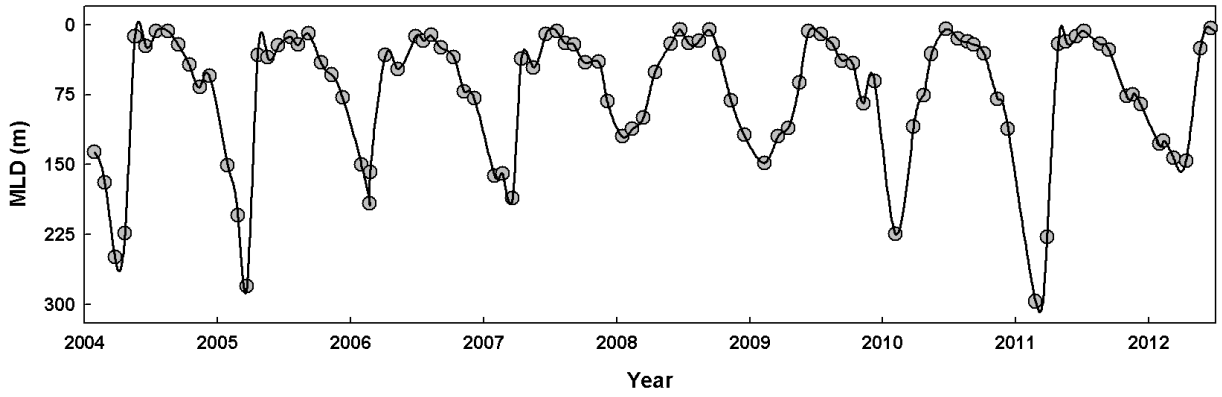

Figure 3. Mixed layer depth (MLD) during the sampling period at the BATS site.

3.1.2 C : N : P ratios in POM and TOM

There were no discernible year-to-year trends in the POM stoichiometry (Fig. 2). The amplitude of variation in the C : N : P ratios of POM was less than that in those of TOM. TON : TOP and TOC : TOP ratios showed a decreasing trend throughout the year 2007 ($r^2 = 0.46$, $p < 0.05$), which was due to an increasing trend in TOP concentration in that year (Fig. 1). There was no annual trend in the TOC : TON ratio. Overall, like POM and TOM concentration patterns, there were no long-term sustained changes in TOC : N : P ratios.

3.2 Seasonal variations

3.2.1 Concentrations of POM and TOM

There was greater variability in C and N pools in the 0–25 m range compared to that in the 25–100 m range (Figs. 4 and 5). In the 0–25 m depth range, TOC showed an increasing trend after deep mixing during the following 5 months before reaching a plateau ($\sim 67\,\mu mol\,kg^{-1}$). POC increased in the first month after deep mixing and then decreased during the next 2 months and remained constant ($\sim 2\,\mu mol\,kg^{-1}$) for the rest of the year (Fig. 4a). The pattern in PON was similar to POC, while those in TON and TOC were opposite to each other during the first 2 months after mixing and then increased until the sixth month (Fig. 4a, b). These higher values of TOC and TON (observed in both the 0–25 and the 25–100 m depth segments) in the sixth month might be attributed to the higher occurrence of *Trichodesmium* colonies during August at BATS (Orcutt et al., 2001; Singh et al., 2013). TOP and POP increased during and 1 month after the deep mixing in the 0–25 m depth range (Fig. 4c). Some of these trends (e.g., higher values of TOC and TON in the sixth month) were also apparent in the 25–100 m depth range but were not as prominent as in the 0–25 m depth range (Figs. 4 and 5).

3.2.2 C : N : P ratios in POM and TOM

TON : TOP (68 ± 9) and PON : POP (36 ± 11) values were greater than the Redfield ratio ($p < 0.05$) (Table 1). Patterns in the TOC : TOP and TON : TOP ratio, on the one hand, and in POC : POP and PON : POP, on the other, were similar to each other (Fig. 6a, b). TOC : TOP (983 ± 168) and POC : POP (210 ± 67) values were much higher than the Redfield ratio of 106 ($p < 0.05$). TOC : TON (15 ± 0.5) increased for the 2 months following deep mixing and decreased until the seventh month (Fig. 6c). POC : PON (6 ± 3) increased in the month after deep mixing but remained around the Redfield ratio throughout the year. Minimal variability in concentration and ratios in the 25–100 m depth range suggests confinement of the more dynamic biogeochemical processes to within the mixed layer, i.e., to within 0–25 m (Figs. 5 and 7).

3.2.3 N : P ratios in inorganic nutrients

The average $NO_3^- : PO_4^{3-}$ ratio was 25.6 ± 9.1 in the 100–500 m depth range at BATS, which is greater than the Redfield ratio (Table 1). We excluded data from the top 100 m in this analysis due to low precision relative to the mean nutrient values, which are at or near analytical detection limits due to active biological uptake. NO_3^- and PO_4^{3-} were at their highest concentrations before deep mixing and decreased immediately following the month of deepest mixing and remained constant for the rest of the year (Fig. 8). The decrease in NO_3^- and PO_4^{3-} concentrations was likely due to dilution with low-nutrient surface water during mixing.

3.2.4 N : P ratios in the particulate flux at 200 m

The PON fluxes increased during and peaked immediately after winter mixing, while POP fluxes showed elevated values before and shortly after the time of deep mixing (Fig. 8). The N : P ratio of export fluxes was nearly twice that of the

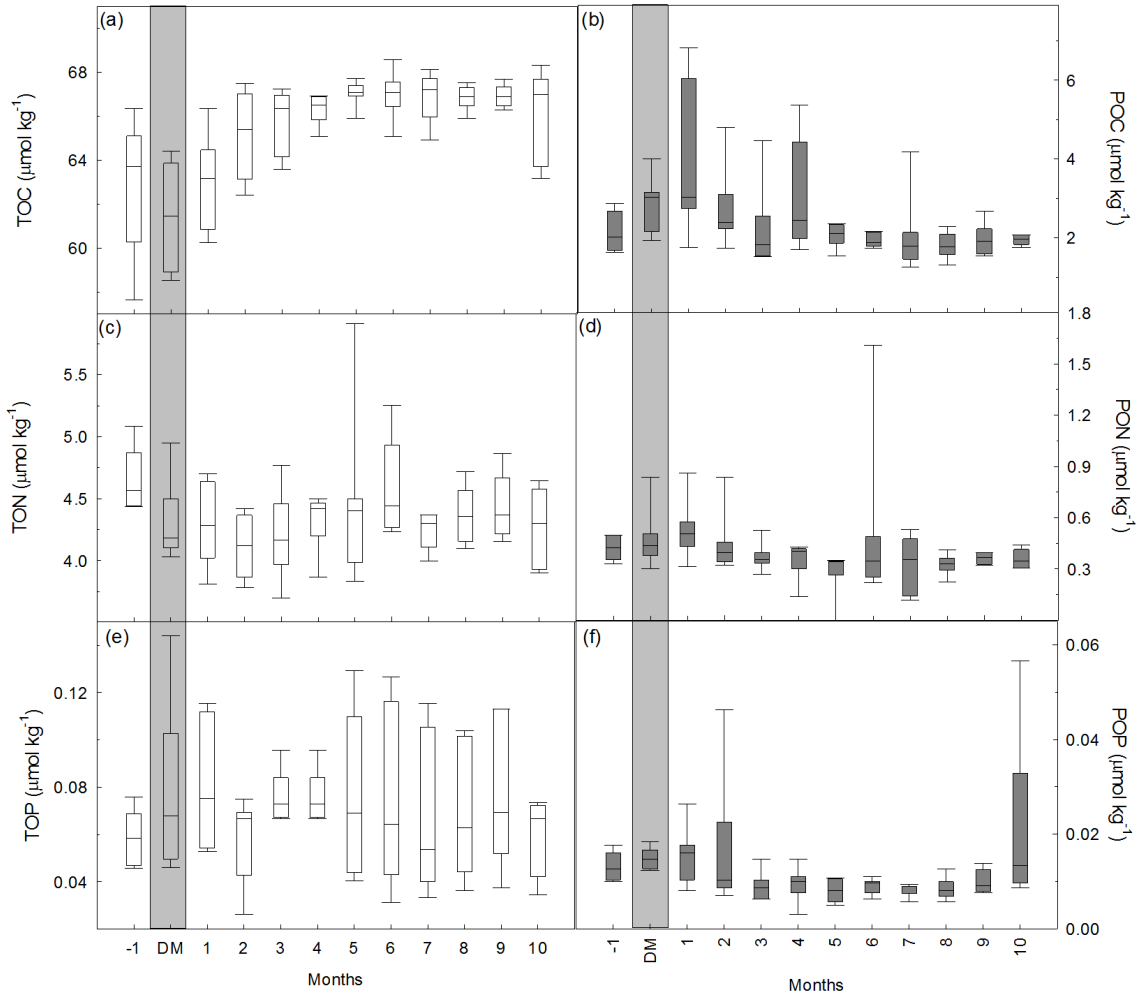

Figure 4. Box–whisker plot comparing the annual concentrations of total (open bars) and particulate organic matter (filled bars) relative to the deep mixing at a depth of 0–25 m at BATS (data used are from January 2005 to December 2011). Bottom and top of the box define the 25 and 75 % data distribution, and the error bars define the 5 and 95 % data distribution. The dark gray vertical bar represents the period of deep mixing (DM) for each year.

PON : POP ratio in the suspended matter (upper 100 m; Table 1).

3.2.5 Chlorophyll *a* and phytoplankton cell abundance

Chlorophyll *a* values decreased after the spring bloom that was stimulated by deep mixing (Fig. 9a). *Prochlorococcus* was dominant during the oligotrophic period of the year, while these were least abundant around the time of deep mixing (Fig. 9b). In contrast, *Synechococcus* and picoeukaryotes were more abundant during the more productive season (Fig. 9c,d) and followed the annual pattern in chlorophyll *a*. There was no discernible seasonal pattern in nanoeukaryote abundance (Fig. 9e).

4 Discussion

From the approximately 8 years of BATS data presented here, it is apparent that the total and particulate-organic matter C : N : P stoichiometries are not a long-term fixed ecosystem property but vary seasonally and deviate substantially from the canonical Redfield ratio. Observed C : N : P ratios in TOM and POM were much greater than the Redfield ratio, averaging 983 : 68 : 1 and 210 : 36 : 1, respectively, for the entire data set (Figs. 2, 4, 5).

4.1 Connections among POM, TOM and inorganic nutrients

Redfield hypothesized what was effectively a two-box model of nutrients shuttling between particulate and dissolved forms. However, there are a number of different biological,

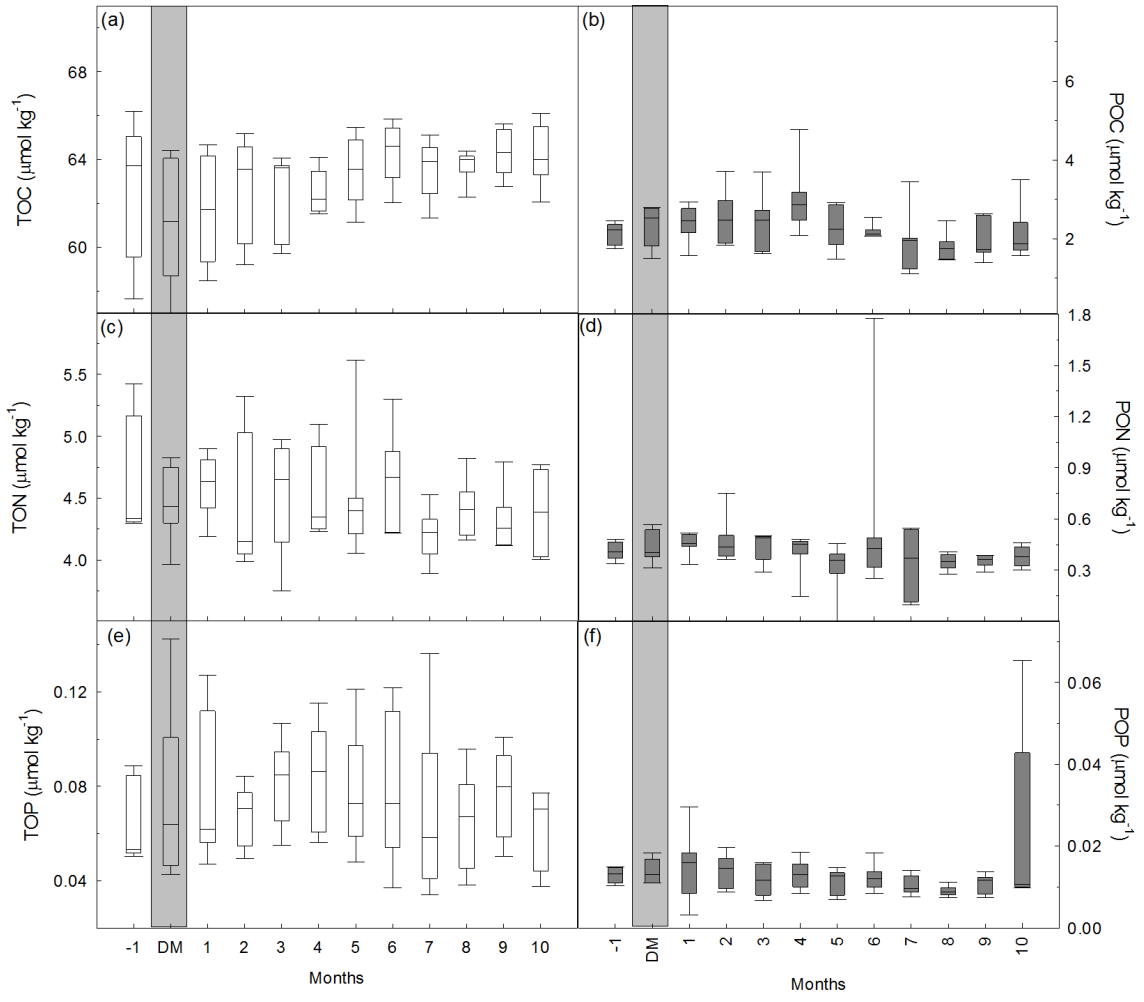

Figure 5. Box–whisker plot comparing the annual concentrations of total (open bars) and particulate (filled bars) matter relative to the deep mixing at a depth of 25–100 m (data used are from January 2005 to December 2011). All else as in Fig. 4.

chemical and physical processes acting on particles as they settle throughout the water column. Higher N : P ratios in the particulate fluxes than in the suspended matter could be due to the preferential export of N or to preferential remineralization of P, but similar C : N ratios in the fluxes and suspended matter would lend more support to the latter scenario (Figs. 4, 8; Table 1; Monteiro and Follows, 2012). The N : P ratio of export fluxes was also generally more than twice that of the dissolved $NO_3^- : PO_4^{3-}$ ratio at depth (Fig. 8c). The preferential remineralization of P from settling material could potentially explain this difference, as there is little evidence for N loss in this well-oxygenated region; however the advective flux of low-$NO_3^- : PO_4^{3-}$ waters needs to be considered. Indeed, the literature indicates that subeuphotic waters at BATS are a mixture of water which originated to the north of the site, which has characteristically low $NO_3^- : PO_4^{3-}$ ratios (Bates and Hansell, 2004; Singh et al., 2013). The processes of remineralization are not direct from particulate to inorganic pools, and, indeed, cycling through the dissolved organic pool, which dominates TOM, is important. One explanation for the TON : TOP ratio being greater than the Redfield ratio is that TON is less reactive than TOP and broken down mainly in the subsurface layer (Letscher et al., 2013), while TOP is labile or semi-labile and both remineralized and assimilated at a shallower depth (Björkman et al., 2000). Consequently, TOP has faster turnover times (Clark et al., 1998). In contrast to this interpretation, our observations suggest that TON and TOP values increase slightly with depth, suggesting a net (i.e., remineralization exceeding assimilation) flow of material from the particulate organic pool to the dissolved organic pool for both elements (comparing data in Figs. 4 and 5).

Our results on the TON : TOP ratio have important implications for the ocean biogeochemistry of oligotrophic waters where dissolved organic nitrogen (DON) and phosphorus (DOP) concentrations in the sunlit layers exceed the concentration of inorganic nutrients by 1 order of magnitude. Dissolved organic pools are essential in sustaining phytoplank-

Table 1. Average concentration ($\mu mol\,kg^{-1}$), molar ratio of various biogeochemical parameters and particle fluxes ($mmol\,m^2\,d^{-1}$) from the BATS data presented in Fig. 1.

Concentration (C) in the upper 100 m			
Parameter	$C \pm \sigma$ [a]	No. of samples	Sampling period
TOC	63.81 ± 2.86	714	January 2004–December 2011
TON	4.43 ± 0.50	712	January 2004–December 2011
TOP	0.07 ± 0.03	547	June 2004–November 2011
POC	2.36 ± 1.14	844	January 2004–April 2012
PON	0.40 ± 0.19	845	January 2004–April 2012
POP	0.01 ± 0.01	696	January 2004–April 2012
Ratio (R)[b] in the upper 100 m			
Parameter	$R \pm \sigma$	No. of data points[c]	Sampling period
TOC : TON	15 ± 0.5	86	July 2004–December 2011
POC : PON	6 ± 3	95	January 2004–April 2012
TON : TOP	68 ± 9	77	July 2004–November 2011
PON : POP	36 ± 11	88	January 2004–April 2012
TOC : TOP	983 ± 168	78	July 2004–November 2011
POC : POP	210 ± 67	88	January 2004–April 2012
Inorganic nutrient stoichiometry in 100–500 m			
Parameter	(C or R) $\pm \sigma$	No. of data points	Sampling period
NO_3^-	2.74 ± 2.40	3425	October 1988–July 2012
PO_4^{3-}	0.11 ± 0.13	3405	October 1988–July 2012
$NO_3^- : PO_4^{3-}$	25.6 ± 9.1	2415	October 1988–July 2012
Particle fluxes at 200 m			
Parameter	$C \pm \sigma$	No. of samples	Sampling period
C	1.68 ± 1.07	254	January 1989–December 2011
N	0.23 ± 0.16	254	January 1989–December 2011
P	0.008 ± 0.014	64	October 2005–December 2011
Ratio in particle fluxes at 200 m			
Parameter	$R \pm \sigma$	No. of data points	Sampling period
N : P	57 ± 46	61	October 2005–December 2011
C : P	287 ± 269	62	October 2005–December 2011
C : N	7.9 ± 2.8	252	January 1989–December 2011

[a] σ is standard deviation of the samples mentioned in next the column. [b] Ratios and their standard deviations are derived from the monthly mean values; [c] one datum would be the mean of many values a particular month of the concentration in the upper 100 m.

ton growth in these regions (Church et al., 2002; Williams and Follows, 1998). Nutrient levels determine phytoplankton growth and their stoichiometry (Klausmeier et al., 2004); TON : TOP in the oligotrophic regions might be more relevant to determine the optimal N : P stoichiometry of phytoplankton than the ratio of inorganic pools alone.

4.2 Linkages of concentrations and ratios of POM and TOM to chlorophyll *a* and phytoplankton

We hypothesize that C : N : P ratios in the aggregated phytoplankton community itself change the elemental stoichiometry of the POM and TOM pools. The C : N : P ratio is different in different phytoplankton communities, and their biological uptake and degradation could potentially change the elemental stoichiometry of the particulate and dissolved organic matter. The C : N : P ratio varies geographically and its pattern correlates with global variations in temperature, overall

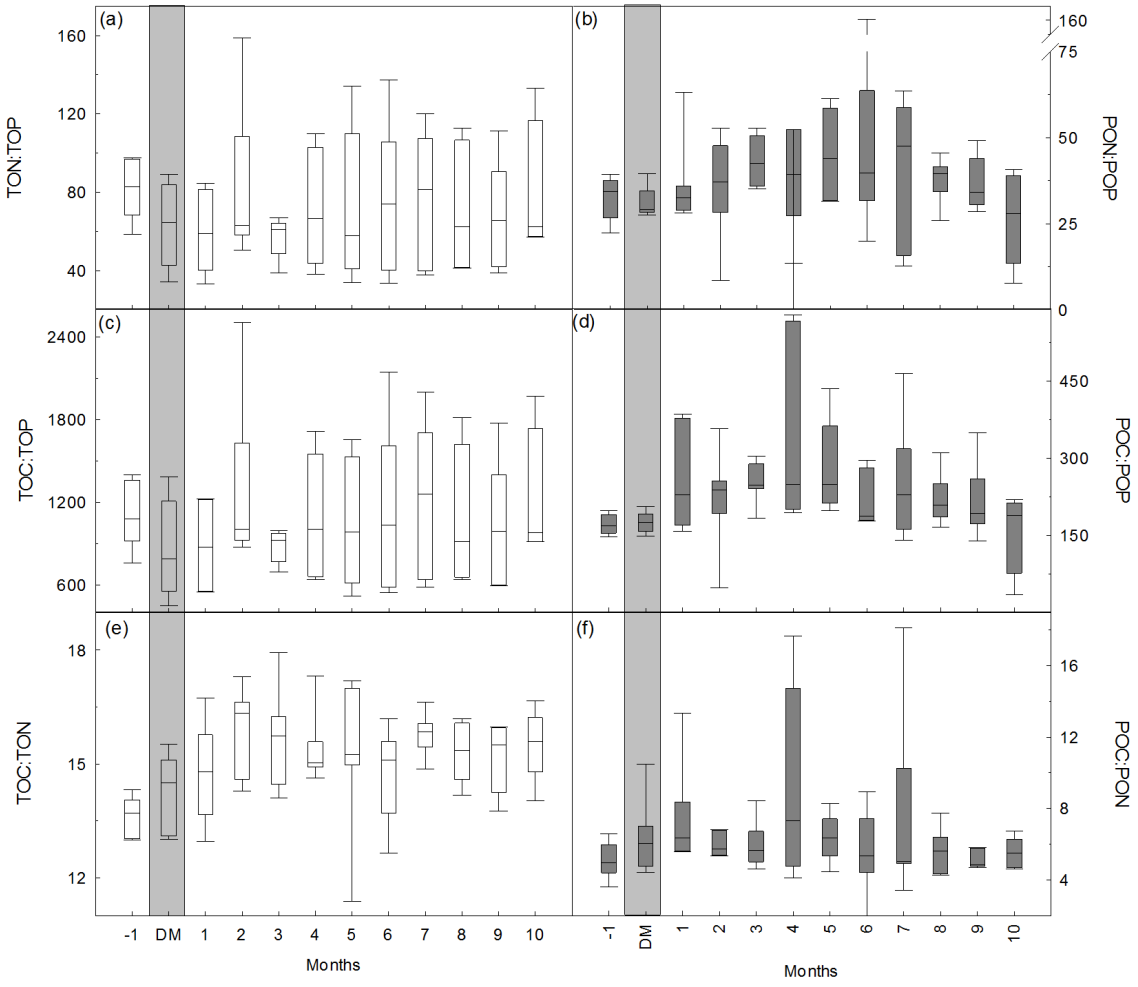

Figure 6. Box–whisker plot comparing the annual ratios of elemental stoichiometry relative to the deep mixing at a depth of 0–25 m (data used are from January 2005 to December 2011). All else as in Fig. 4.

nutrient concentrations and phytoplankton functional groups. These latitudinal patterns in the C : N : P ratio have been attributed to changes in phytoplankton community as polar (colder) regions have a high abundance of diatoms with low N : P and C : P ratios, in contrast to the directly measured high elemental ratios in cyanobacteria from warmer regions (Martiny et al., 2013). So how and why does the C : N : P ratio vary in phytoplankton communities? Two mechanisms could explain the variability in the C : N : P ratios in a phytoplankton community. The first mechanism suggests that the taxonomic composition of a phytoplankton community influences its elemental composition. Elemental ratios inside a cell are controlled by growth strategies (Klausmeier et al., 2004) . Studies have reported low C : P and N : P ratios in fast-growing diatoms (e.g., Price, 2005), whereas slower-growing cyanobacteria have C : P and N : P ratios higher than the Redfield ratio (Bertilsson et al., 2003; Martiny et al., 2013). More precisely, it is not so much the growth rate that determines the difference but the machinery invested in nutrient acquisition versus protein production.

The second mechanism links the nutrient supply ratio to a taxonomically "hard-wired" cellular elemental ratio (Rhee, 1978). Chlorophyll *a* values were anticorrelated with TOC values ($r^2 = 0.76$, $p < 0.05$). The gradual increase in chlorophyll *a* during the 4 months before deep mixing is due to similar increase in MLD before deep mixing (Fig. 3), which suggests that there may be an enhanced nutrient flux into the upper layer well before deep mixing (e.g., Fawcett et al., 2014). *Prochlorococcus* and *Synechococcus* profiles were correlated to each other in the first 7 months from the point of deepest mixing ($r^2 = 0.58$, $p < 0.05$), and there was no relation in the rest of the year in the 0–25 m depth range. Furthermore, *Synechococcus* cell abundance was correlated with POC ($r^2 = 0.67$, $p < 0.05$), PON ($r^2 = 0.47$, $p < 0.05$), POP ($r^2 = 0.29$, $p < 0.05$) and anticorrelated with TOC values ($r^2 = 0.72$ $p < 0.05$) in the 0–25 m depth range. *Synechococcus* is more abundant during the more produc-

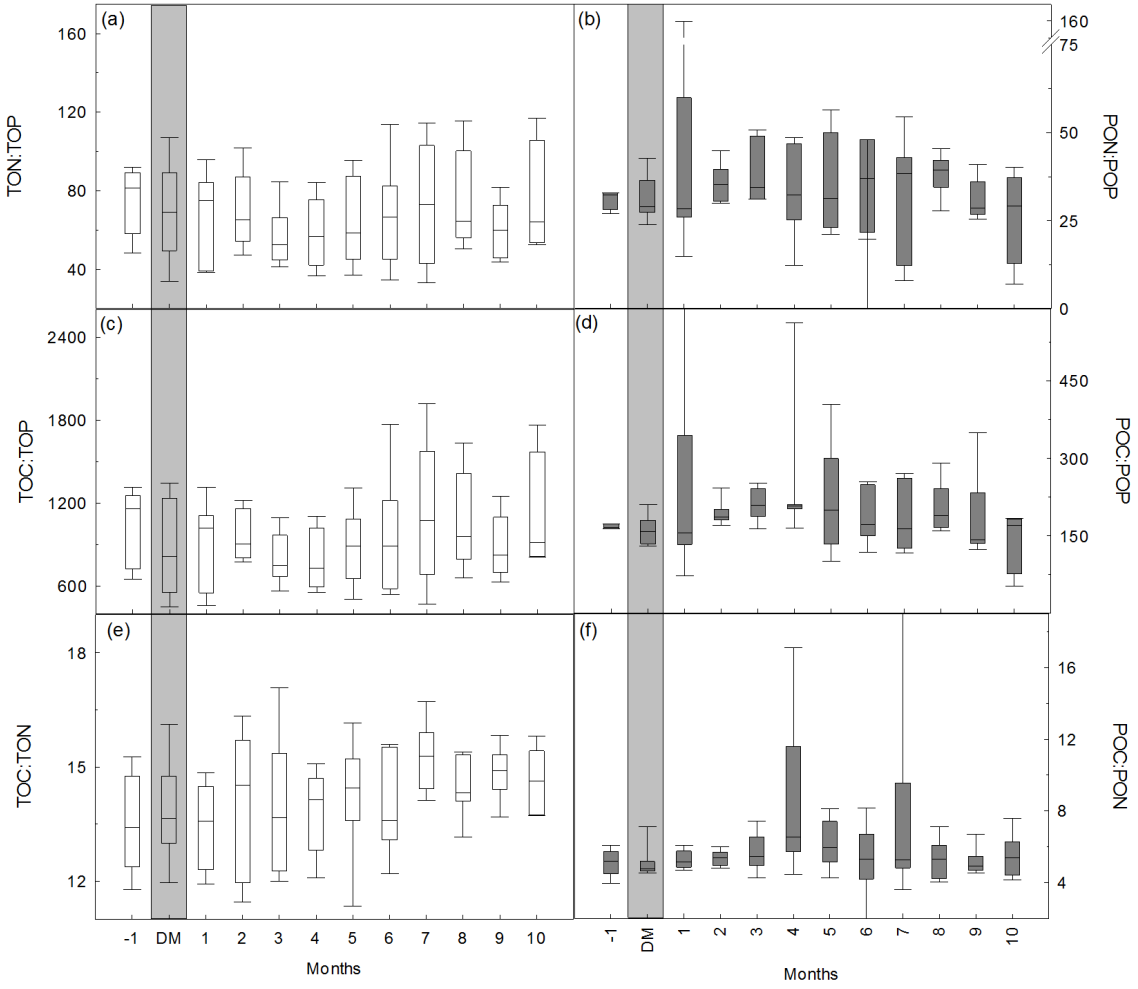

Figure 7. Box–whisker plot comparing the annual ratios of elemental stoichiometry relative to the deep mixing at depth of 25–100 m (data used are from January 2005 to December 2011). The gray bar represents the period of deep mixing (DM) for each year. All else as in Fig. 4.

tive season, whereas *Prochlorococcus* is dominant during the highly oligotrophic part of the year. Such patterns are typically observed in many parts of the ocean. The seasonal pattern of picoeukaryote abundance was similar to that of *Synechococcus* ($r^2 = 0.58$, $p < 0.05$) and chlorophyll *a* ($r^2 = 0.81$, $p < 0.05$). POC : PON : POP ratios in *Prochlorococcus*, *Synechococcus* and picoeukaryote are 234 : 33 : 1, 181 : 33 : 1 and 118 : 15 : 1, respectively, at the BATS site (Martiny et al., 2013, and Lomas et al., unpublished data), which clearly suggests imprints of a mixture of *Prochlorococcus* and *Synechococcus* on the observed POM stoichiometry presented in Table 1. The biomass of *Prochlorococcus*, *Synechococcus* and picoeukaryotes together contributes ∼ 40 % to the POC pool (Casey et al., 2013) and ∼ 75 % to the PON pool (Fawcett et al., 2011), with major contributions from each group varying seasonally. Hence, variability in biological parameters could potentially explain a significant fraction of the variability in the POM and TOM ratios but not all of it. So what else drives the variability in the C : N : P ratios?

We analyzed trends in the TON : TOP and TOC : TOP ratios for December 2006 to January 2008 data, along with phytoplankton cell abundances for the top 100 m BATS data. Since the variation in TON : TOP and TOC : TOP were due to an increasing trend in TOP, we correlated TOP concentrations with a lag of 3 months (there is a time lag between phytoplankton and elemental abundance, as observed by Singh et al., 2013) in phytoplankton cell abundances (data from September 2006 to November 2007; Fig. 10a). We observed a significant anticorrelation ($r^2 = 0.61$, $p < 0.001$) between nanoeukaryotes and TOP but the data did not correlate with other phytoplankton groups (Fig. 10a). Given the paucity of elemental composition data regarding nanoeukaryotes, we hypothesize that these cells have a high requirement for P and potentially meet that requirement by assimilating TOP.

We further analyzed this increasing trend in the TOP concentration with climate indices. The Arctic Oscillation is a major climatic phenomenon in the North Atlantic Ocean (Thompson and Wallace, 1999). Positive trends in the Arc-

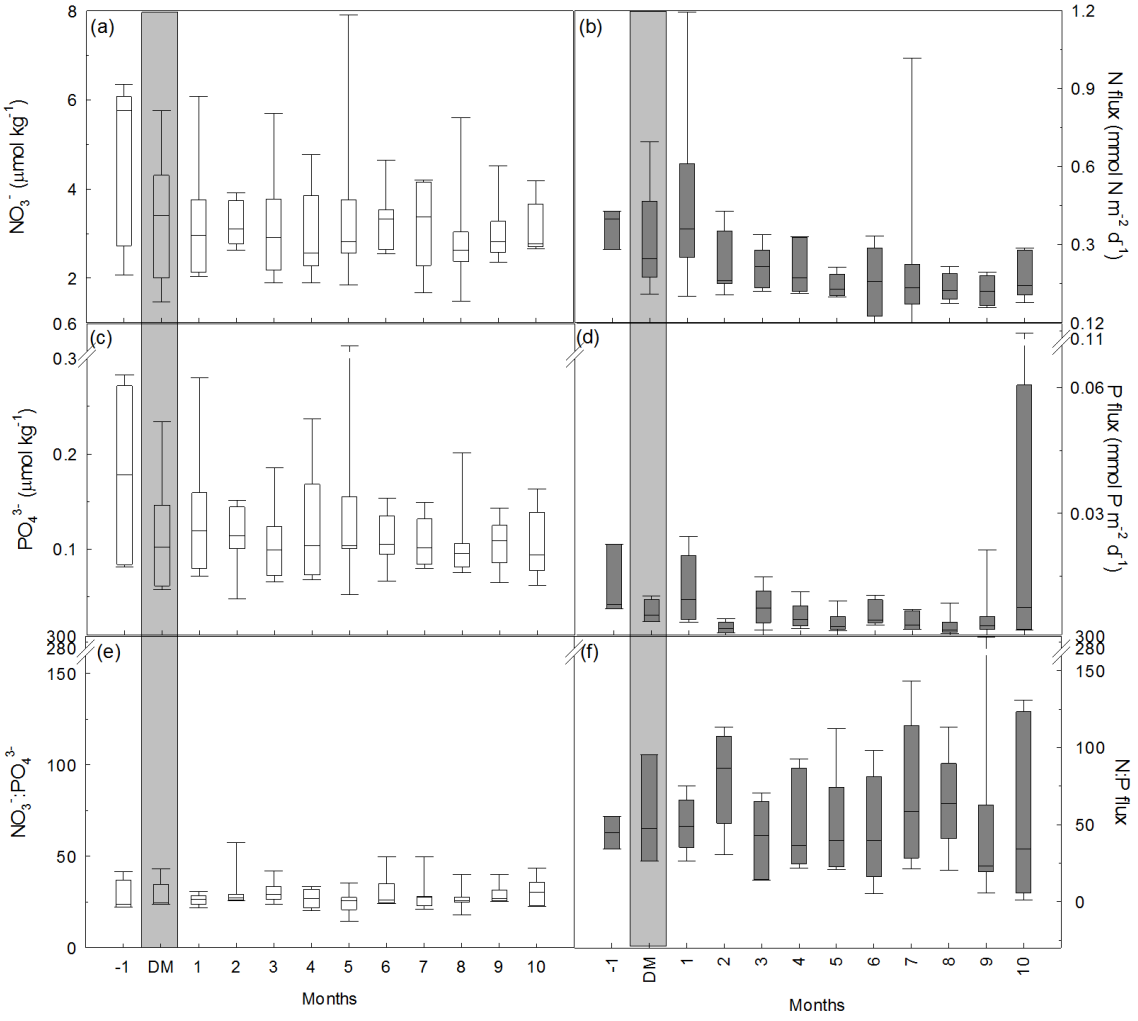

Figure 8. Box–whisker plot comparing the annual variation in NO_3^- and PO_4^{3-} and their ratio relative to the deep mixing at a depth of 100–500 m (data used are from January 2005 to December 2011). The gray bar represents the period of deep mixing (DM) for each year. All else as in Fig. 4.

tic Oscillation lead to higher temperatures, advanced spring, and increased CO_2. This could lead to enhanced uptake of CO_2 during spring as has been found in terrestrial systems (Schaefer et al., 2005). Higher buildup of organic matter would require more P, and hence we correlated TOP concentration with the monthly Arctic Oscillation index with a lag of 1 year (monthly Arctic Oscillation indices are from November 2005 to December 2006 because there is a lag of 1 year before climatic oscillations in the North Atlantic show their impact on surface biogeochemistry; Fromentin and Planque, 1996). We observed a significant correlation ($r^2 = 0.46$, $p < 0.01$) between the Arctic Oscillation and TOP concentrations (Fig. 10b). Since variations in phytoplankton cell abundances and climate variability could not explain all the variation in the elemental stoichiometry, other mechanisms are yet to be identified to explain the observed variability in the elemental stoichiometry.

4.3 Role of DOM in microbial carbon export

Many biogeochemical model estimates of export production assume Redfield stoichiometry in export fluxes, but a non-Redfieldian approach has become more popular recently (Letscher and Moore, 2015). Export production is estimated to be 3–4 mol C m^{-2} yr^{-1} in the BATS region (Jenkins, 1982; Emerson, 2014), which requires more nutrient input than observations suggest (Williams and Follows, 1998). A possible mechanism to sustain such export production is the supply of DOM to the sunlit layer.

DOM consists of complex compounds whose chemical characterization is incomplete, but it is evident that DOM elemental stoichiometry differs drastically from the Redfield ratio. Differential production and degradation of DON and DOP with lifetimes comparable to the gyre circulation could potentially change the overall stoichiometry of nutrient sup-

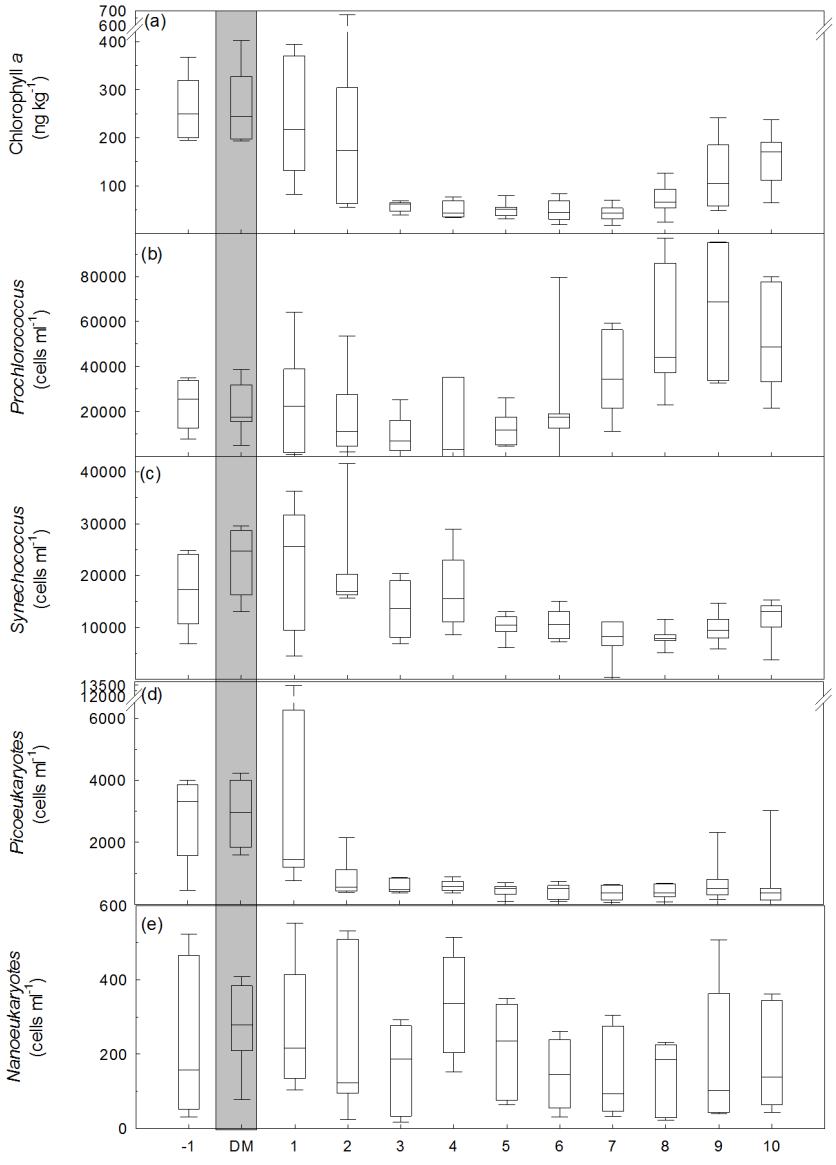

Figure 9. Box–whisker plot comparing the annual variation in chlorophyll *a* and cell counts for *Prochlorococcus*, *Synechococcus*, picoeukaryotes, and nanoeukaryotes relative to the deep mixing at a depth of 0–25 m at BATS (data used are from January 2005 to December 2011). The gray bar represents the period of deep mixing for each year. All else as in Fig. 4.

ply (Voss and Hietanen, 2013). Preferential degradation of DOP rather than DON expands the niche of diazotrophs beyond that created by subsurface denitrification. Diazotrophs can quickly utilize recycled DOP (Dyhrman et al., 2006). Simultaneously, these diazotrophs release DON (Mulholland, 2007), which can be used by other phytoplankton, but this DON likely has associated DOP. In the P-stressed Sargasso Sea, DOP contributes up to 50 % of P demand for primary production (Lomas et al., 2010) and up to 70 % to the exported POP (Roussenov et al., 2006; Torres-Valdés et al., 2009). Indeed, a 1-D biogeochemical model for BATS that included an explicit DOP pool and a generic DOM pool significantly improved the capture of natural variability in both particulate (suspended and exported) and dissolved (organic and inorganic) pools (Salihoglu et al., 2007). These model results, as well as others connecting DOP cycling to particulate-P export (e.g., Roussenov et al., 2007), suggest a strong need for direct rate measurements of DOM production and assimilation (e.g., Mahaffey et al. 2014).

5 Conclusions

Our time-series analysis suggests temporal and depth variability in the C : N : P ratio in the Sargasso Sea. C : N : P ratios in TOM were significantly higher than the canonical

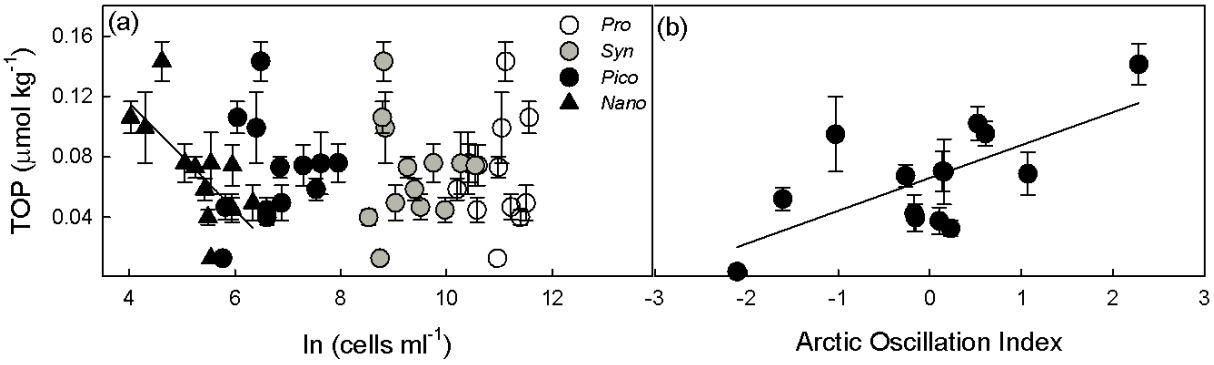

Figure 10. Relationship between TOP (December 2006–January 2008) and **(a)** cell abundances (natural log transformed) of *Prochlorococcus*, *Synechococcus*, picoeukaryotes and nanoeukaryotes during September 2006–November 2007. Among cell abundances, only nanoeukaryotes showed a significant relationship with TOP ($r^2 = 0.61$, $p < 0.001$). Panel **(b)**: relationship between TOP and the Arctic Oscillation index during November 2005–December 2006 ($r^2 = 0.46$, $p < 0.01$).

Redfield ratio, while C : N was similar to the Redfield ratio in the POM. We observed seasonal variability in stoichiometry, but on average the TOC : TON : TOP ratio was 983 : 68 : 1 and the POC : PON : POP was 210 : 36 : 1. Seasonal variation in POM stoichiometry appears to be largely driven by the growth of *Synechococcus* during winter mixing, while the flourishing of *Prochlorococcus* cells during the oligotrophic period (fall) could also explain some variability in the stoichiometry. The C : N : P ratio in *Prochlorococcus* cells resembles the observed mean POC:PON : POP ratio at BATS (210 : 36 : 1). The N : P ratio in subsurface inorganic nutrients was also greater (N : P = 26) than the Redfield ratio in this region. We observed a significant decreasing trend in TON : TOP and TOC : TOP during 2007, which was due to an increase in TOP concentration and could have been partly driven by the Arctic Oscillation and a decrease in the relative abundance of nanoeukaryotes. Other causes for the observed variations in the elemental stoichiometry need to be explored; however, this elemental stoichiometry analysis may improve biogeochemical models, which have hitherto assumed Redfield stoichiometry to estimate export fluxes.

Acknowledgements. We sincerely thank the research technicians, project principal investigators, and captains and crew of BATS cruises for their contribution to the data and the National Science Foundation Chemical and Biological Oceanography Programs for continued support of the BATS program through the following awards: OCE 88–01089, OCE 93–01950, OCE 9617795, OCE 0326885, OCE 0752366, and OCE-0801991. This work was financially supported by the Centre of Excellence (CofE) funded by the Nippon Foundation (NF)–Partnership for Observations of the Global Ocean (POGO) and a grant (CP1213) from the Cluster of Excellence 80 "The Future Ocean" to A. Singh.

Edited by: E. Marañón

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